SIMULTANEOUS MECHANICAL AND HEAT ACTIVATION: A NEW ROUTE TO ENHANCE SERPENTINE CARBONATION REACTIVITY AND LOWER CO_2 MINERAL SEQUESTRATION PROCESS COST

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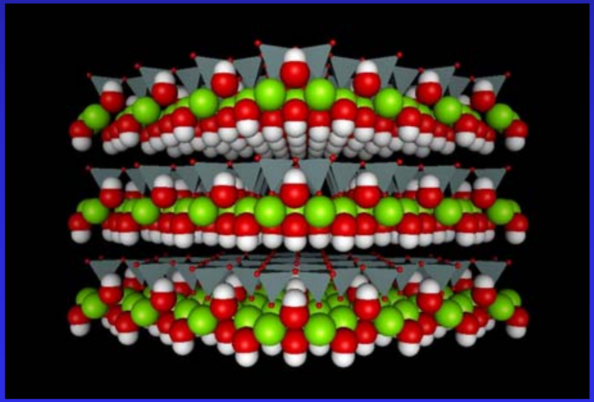

Serpentine (Lizardite): $Mg_3Si_2O_5(OH)_4$

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WHY REDUCE ANTHROPOGENIC CO_2 EMISSIONS?

- **Atmospheric CO_2 levels have increased by 30% over the past two centuries, with most of the increase coming in the past 35 years.**
- **Anthropogenic CO_2 emissions are increasing exponentially.**
- **Scientific debate over the past half decade has shifted from whether or not increasing atmospheric CO_2 levels will impact the global climate, to how soon and at what level will the impact be felt.**

WHAT ARE THE OPTIONS?

- **Short-term:**
  - improved energy generation efficiency
  - inexpensive renewable energy sources
  - forestation/ avoiding deforestation
  - switching from coal to gas

- **Mid to Long-term:**
  - Large-scale renewable energy
  - Nuclear energy
  - CO_2 capture and sequestration combined with fossil fuel/coal energy

CO_2 SEQUESTRATION OPTIONS

Short to Mid-Term:

- Generation of useful materials from CO_2
- Terrestrial Sequestration

Long-term:

- Long-term storage, including:
  - injection into oil/gas reservoirs
    deep confined acquifers
    ocean sites
- Disposal:
  - CO_2 mineral sequestration

SEQUESTRATION VIA MINERAL CARBONATION

AN INTRIGUING CANDIDATE TECHNOLOGY FOR PERMANENT CO_2 DISPOSAL

- **LARGE SCALE:**
  uses Mg-rich minerals (e.g., serpentine and olivine) whose worldwide deposits exceed those needed to carbonate all the CO_2 that can be generated from known global coal reserves.

- **PRODUCES ENVIRONMENTALLY BENIGN PRODUCTS:**
  already naturally abundant.

- **PERMANENT:**
  the products (e.g., magnesite and silica) have proven stable over geological time.

THE PRIMARY CHALLENGE

economically viable process development

SEQUESTRATION VIA MINERAL CARBONATION

THE POTENTIAL FOR ECONOMIC VIABILITY

- **AVOIDS LONG TERM STORAGE COSTS**

  associated with
  - monitoring,
  - sudden release (e.g., insurance and litigation costs), and
  - sequestration to compensate for leakage to the atmosphere.

- **CARBONATION IS EXOTHERMIC:**
  - in principle no energy is required for carbonation to occur.

- **LOW FEEDSTOCK COST:**
  - ~$4-5/ton for mined and milled serpentine.

THE PRIMARY CHALLENGE

To economically accelerate mineral carbonation from a geological to an industrial timescale.

THE CARBON DIOXIDE MINERAL SEQUESTRATION WORKING GROUP

- **MANAGED BY FOSSIL ENERGY, WITH MEMBERS FROM THE**

  - Albany Research Center,
  - Arizona State University,
  - Los Alamos National Laboratory,
  - the National Energy Technology Laboratory,
  - Penn State University,
  - Science Applications International Corporation, and
  - the University of Utah.

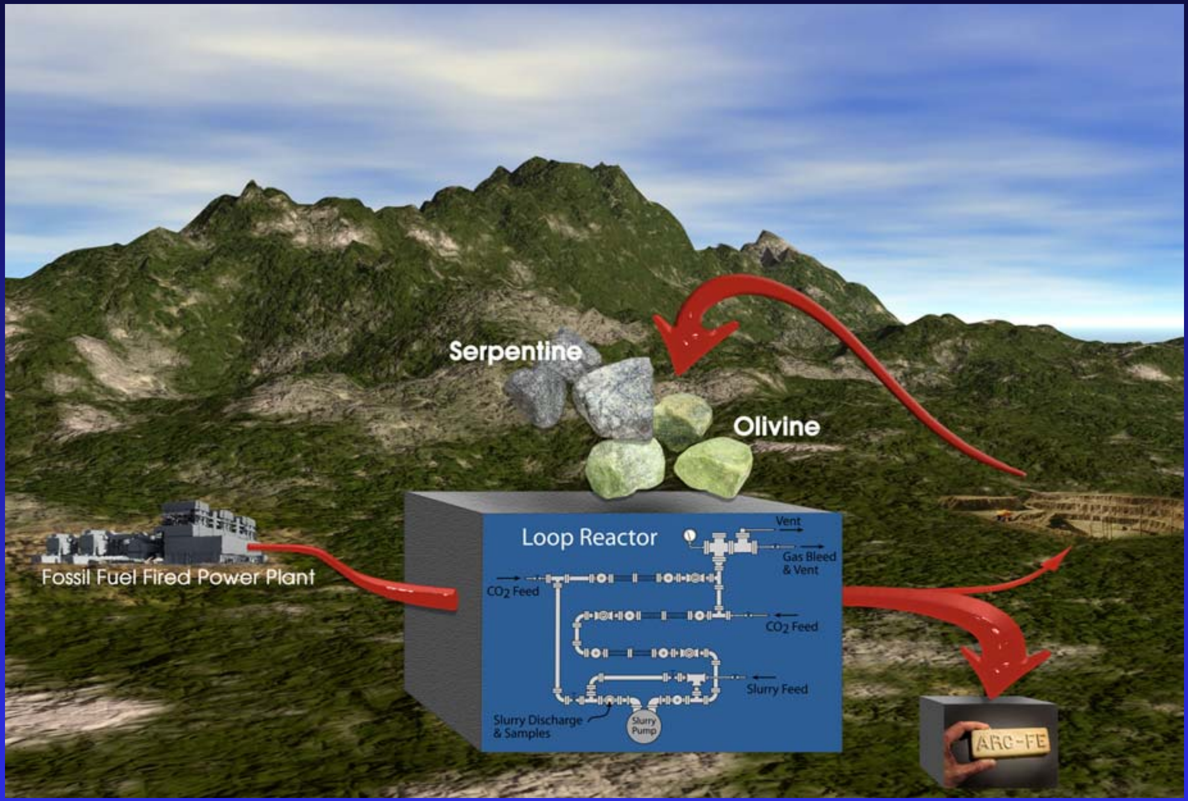
- **PRIMARY GOAL:**

  To explore the potential for economically viable process development

  - accelerating the carbonation process is key:

    1) new process development
    2) cost-effective feedstock activation

THE AQUEOUS MINERAL CARBONATION PROCESS DEVELOPED BY THE ALBANY RESEARCH CENTER (ARC)



Serpentine Carbonation

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \xrightarrow[150\ ^oC\ +\ 150\ atm\ CO_2]{1M\ NaCl\ +\ 0.64\ M\ NaHCO_3} 3MgCO_3 + 2SiO_2 + 2H_2O$$

SERPENTINE FEEDSTOCK ACTIVATION

- Without pretreatment serpentine exhibits poor mineral carbonation reactivity.
- Heat and mechanical activation can effectively enhance serpentine carbonation reactivity (e.g., near complete carbonation in < 1 hr via the ARC process).
- However, these activation processes are not yet economically viable in present form.
- New processes that can further reduce overall process cost are of particular interest.

THERMOMECHANICAL ACTIVATION

A ONE YEAR FEASIBILITY STUDY: THE FIRST 8 MONTHS

MOTIVATION:

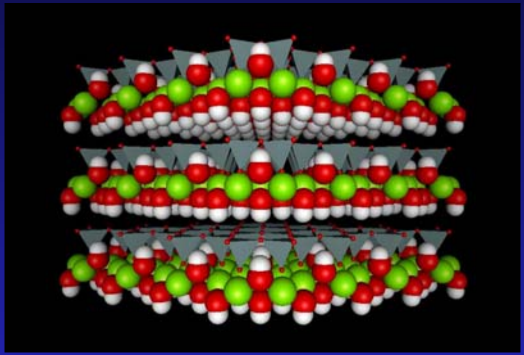
- Power plant waste heat can be used (≤ 250 ^{o}C).
- Mechanical activation waste heat can be used.
- Potential for lower cost feedstock activation.
- Potential to further enhance serpentine reactivity.

OBJECTIVE: to better understand the mechanisms than govern thermo-mechanical activation and its potential to lower process cost.

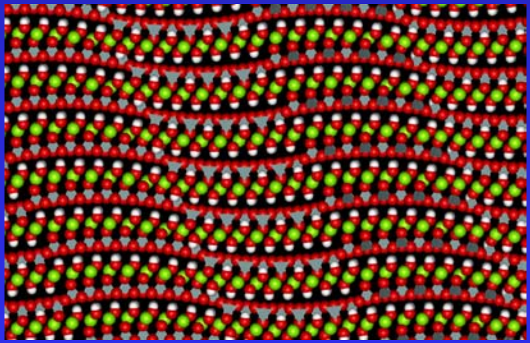
GOAL: to develop the understanding needed to engineer improved materials and processes to enhance carbonation reactivity and lower process cost.

SERPENTINE: STRUCTURALLY AND CHEMICALLY COMPLEX

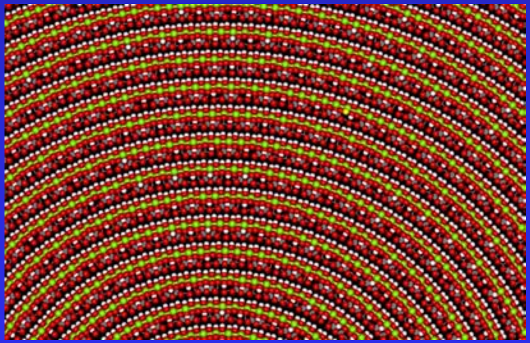
Ideal Composition
$Mg_3Si_2O_5(OH)_4$



Lizardite

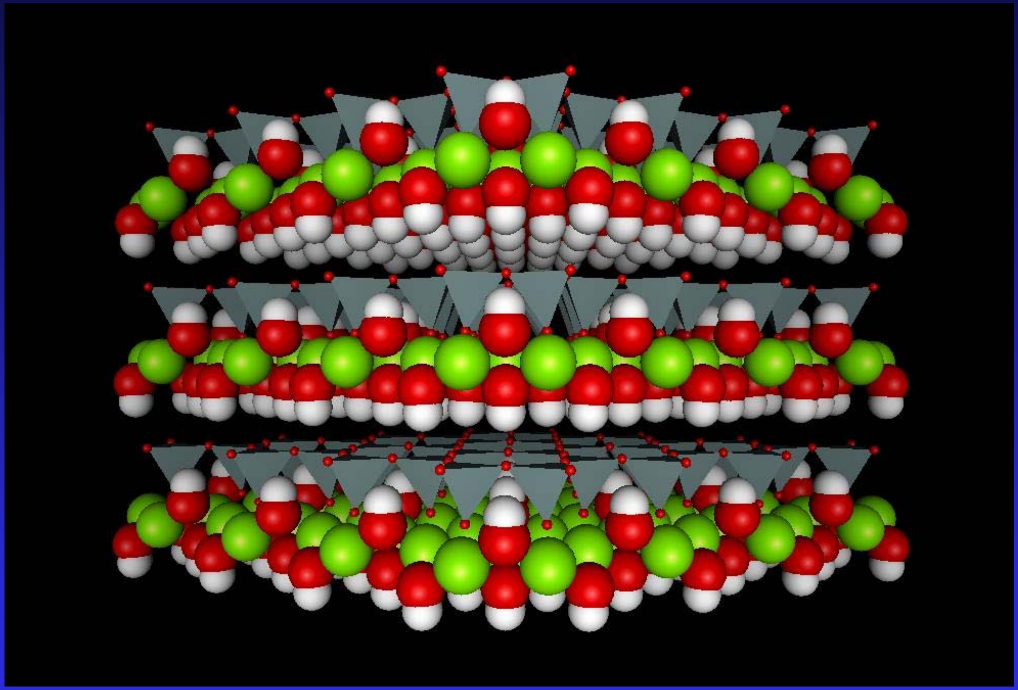


Antigorite



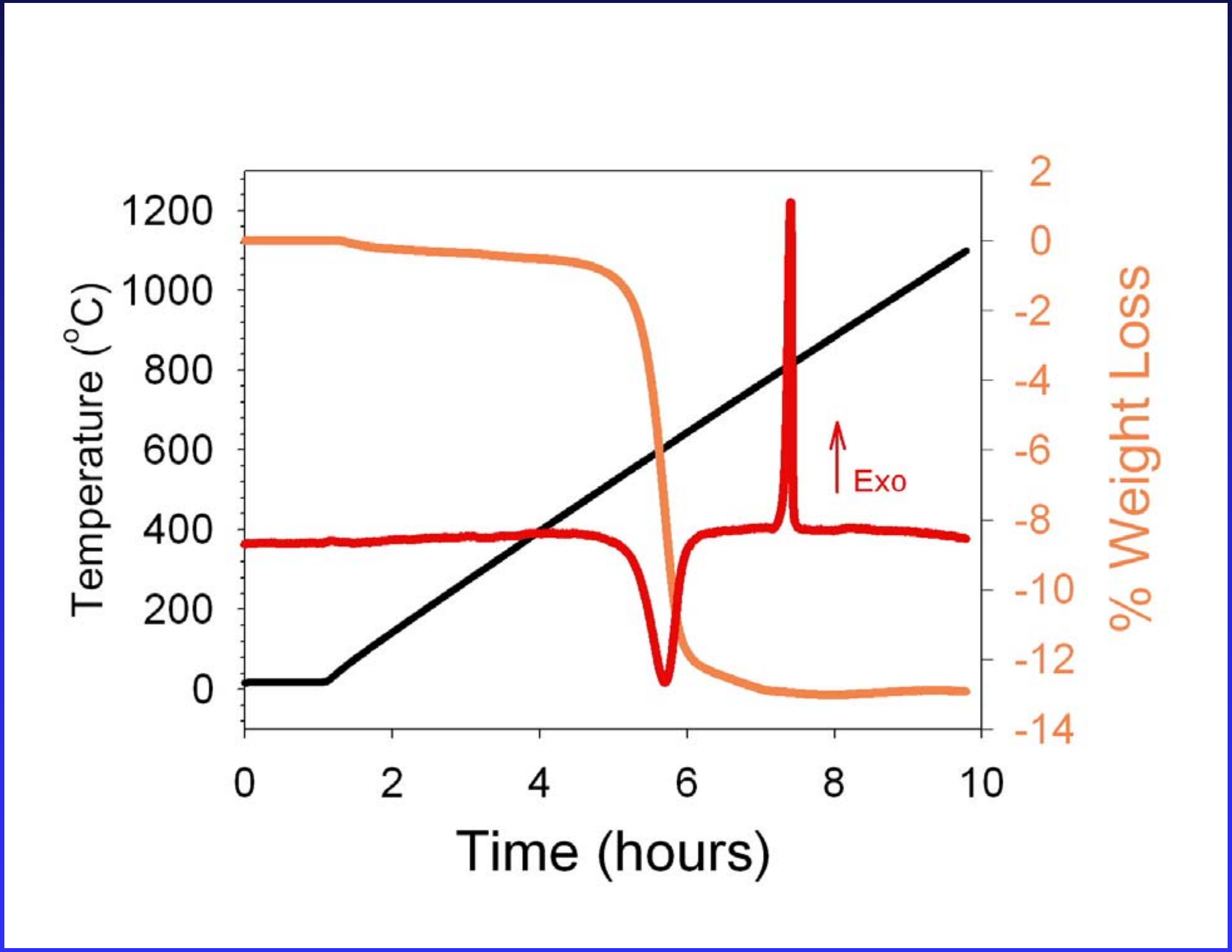
Chrysotile

LIZARDITE: THE SIMPLIST SERPENTINE FOR PROBING THERMOMECHANICAL ACTIVATION

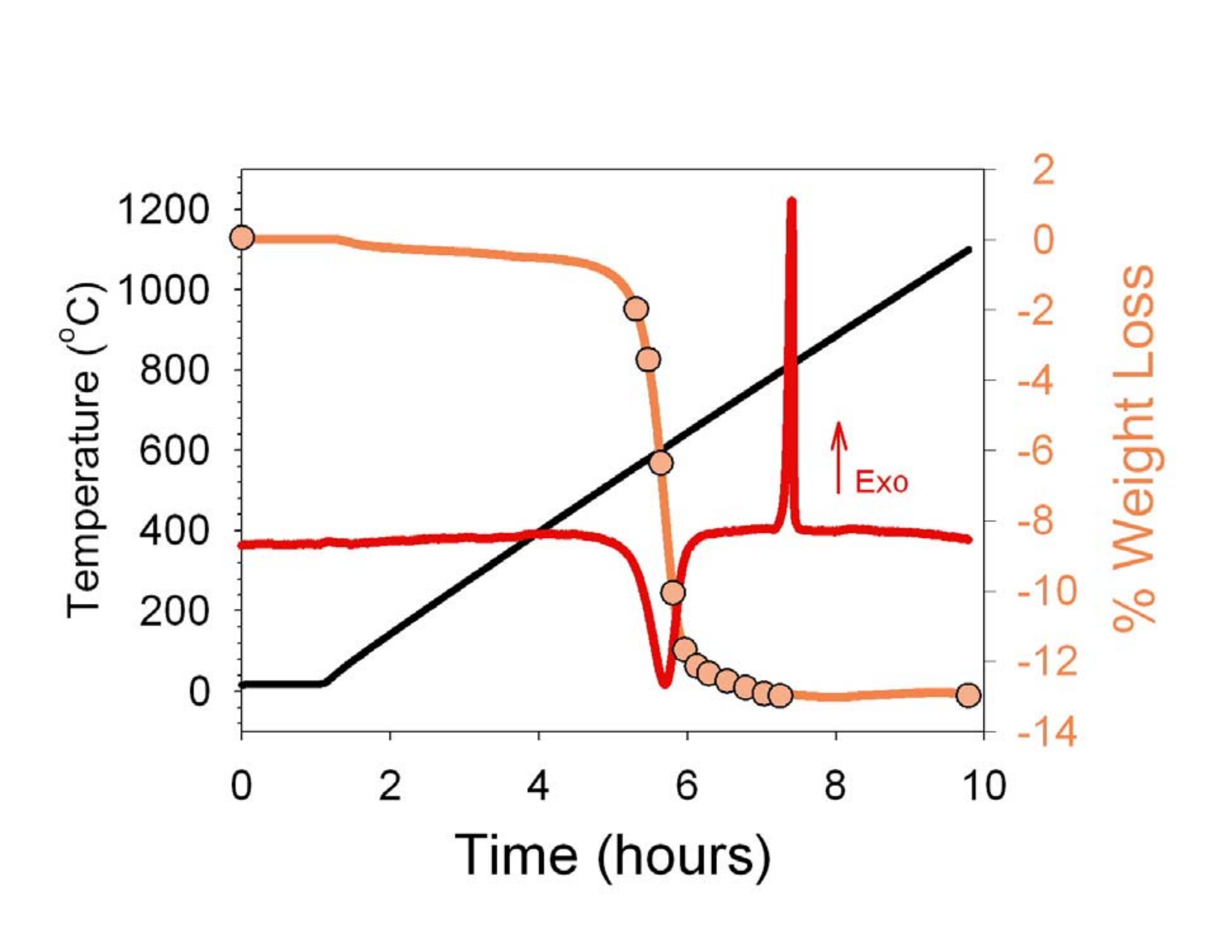


- Two lizardite materials were selected for investigation: Globe lizardite and southwest Oregon lizardite (SWOL).
- SWOL is emphasized to facilitate comparison with previous work done in collaboration with and at the ARC.

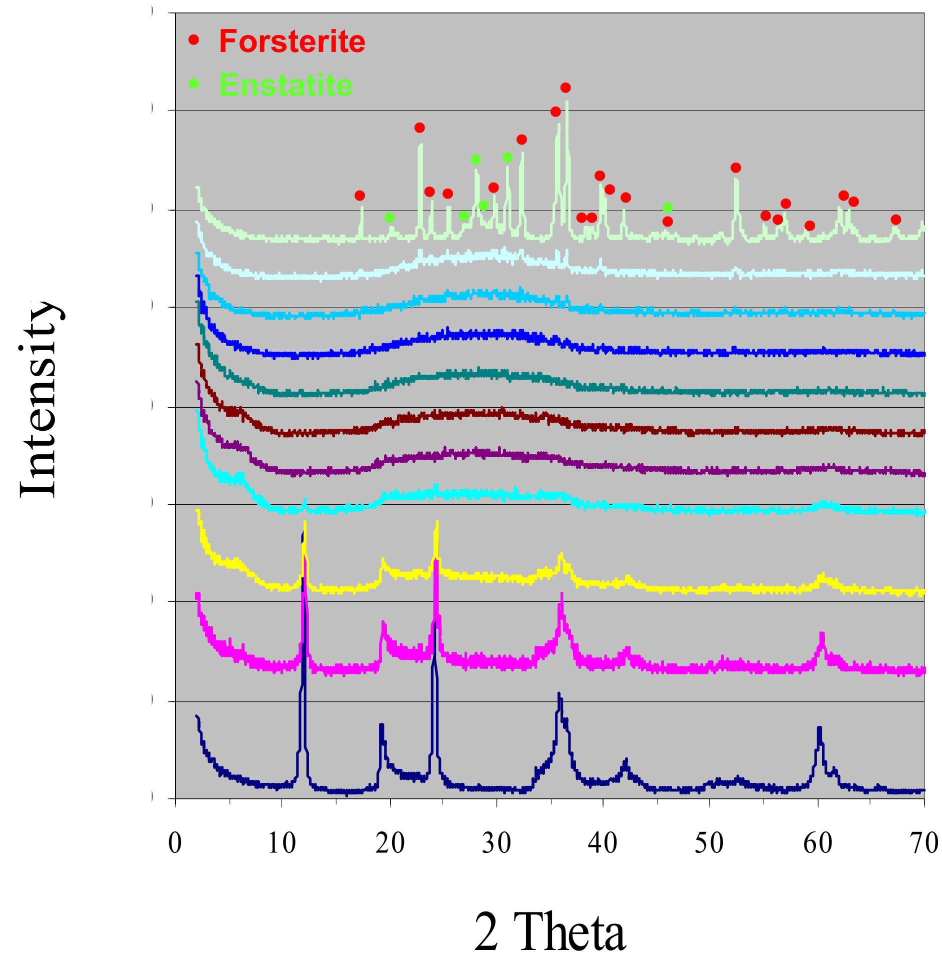
THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS (TGA/DTA) INVESTIGATIONS OF THE LIZADRDITE HEAT ACTIVATION PROCESS



MATERIALS QUENCHED DURING TGA/DTA OF THE LIZARDITE HEAT ACTIVATION PROCESS

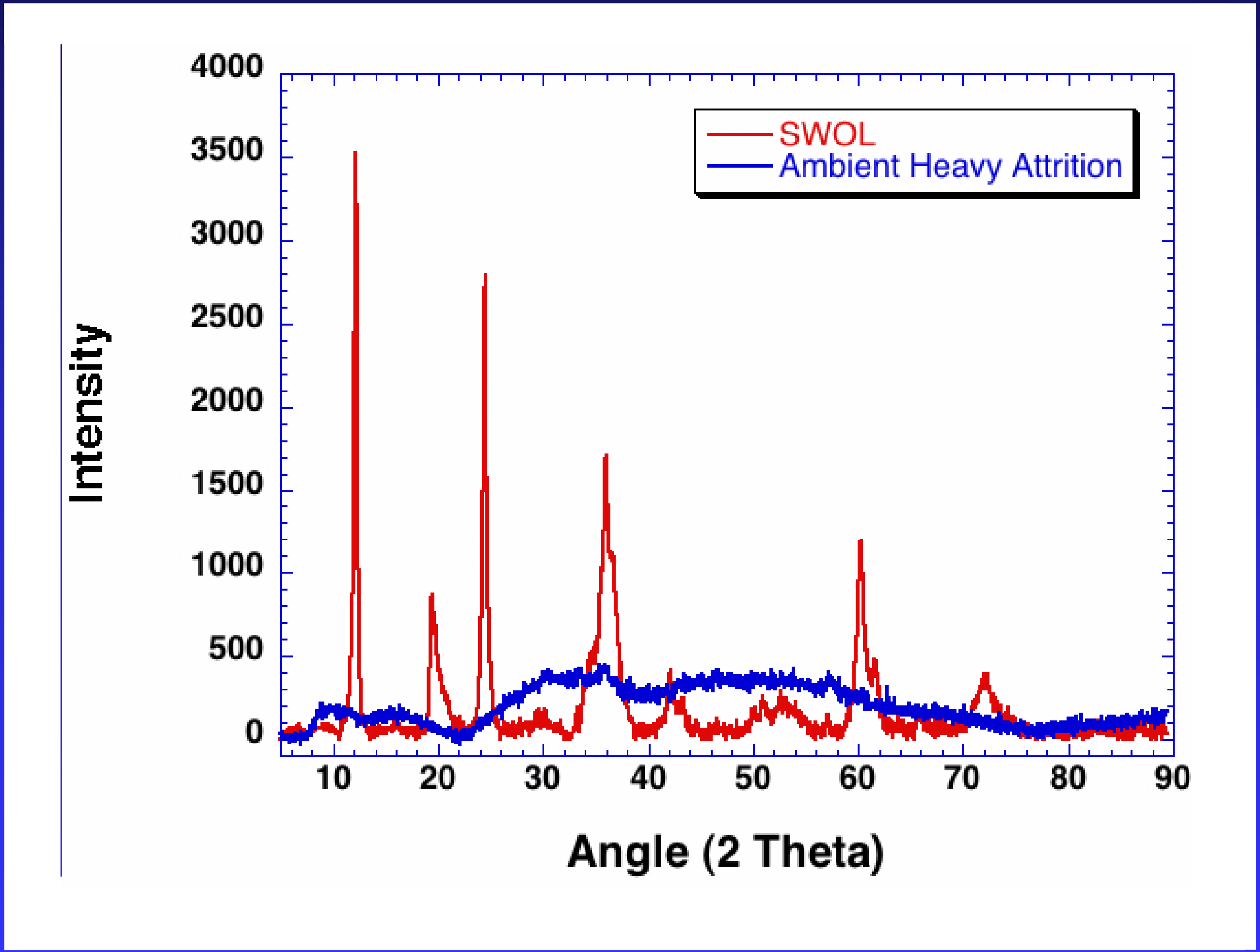


X-RAY POWDER DIFFRACTION ANALYSIS OF LIZARDITE HEAT ACTIVATION



Quench Temp.	Residual Hydroxide
1100ºC	0% OH
795ºC	1% OH
780ºC	2% OH
750ºC	3% OH
710ºC	5 % OH
680ºC	8 % OH
650ºC	10 % OH
610ºC	15 % OH
580ºC	45 % OH
550ºC	75% OH
20ºC	100% OH

X-RAY POWDER DIFFRACTION ANALYSIS OF SOUTHWEST OREGON LIZARDITE (SWOL) MECHANICAL ACTIVATION

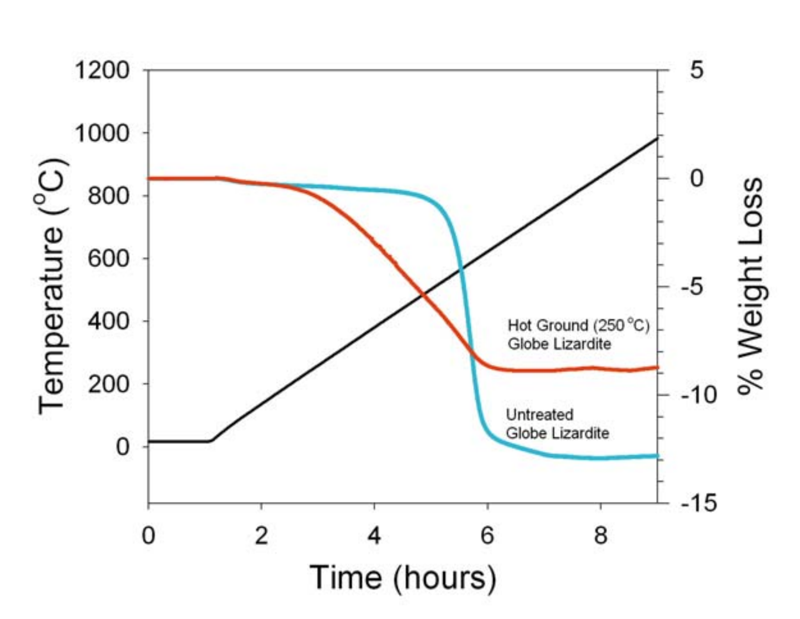


CAN COMBINING THERMAL AND MECHANICAL SERPENTINE PRETREATMENT PROCESSES SYNERGETICALLY ENHANCE ACTIVATION?

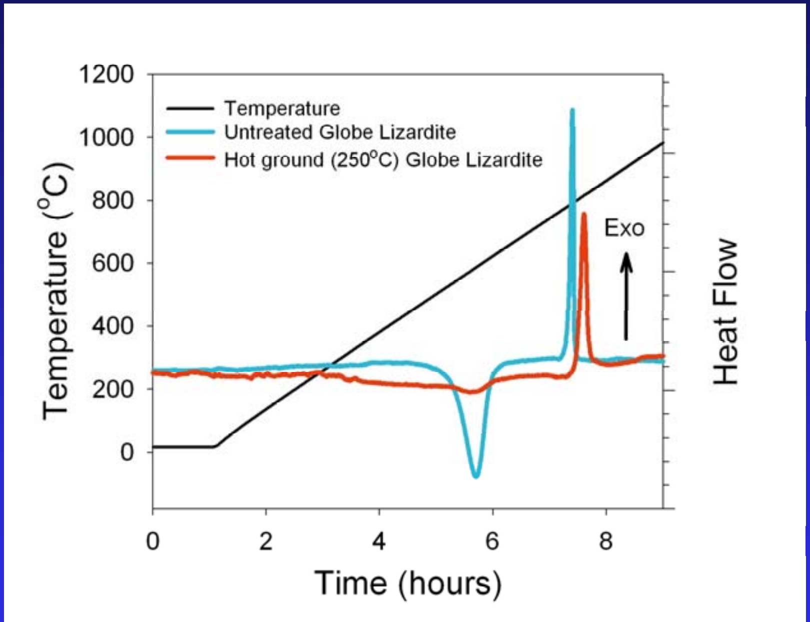
THERMOMECHANICAL ACTIVATION CAPABILITY DEVELOPED AT ARIZONA STATE UNIVERSITY

THERMOMECHANICALLY ACTIVATED GLOBE LIZARDITE

THERMOGRAVIMETRIC ANALYSIS



DIFFERENTIAL THERMAL ANALYSIS



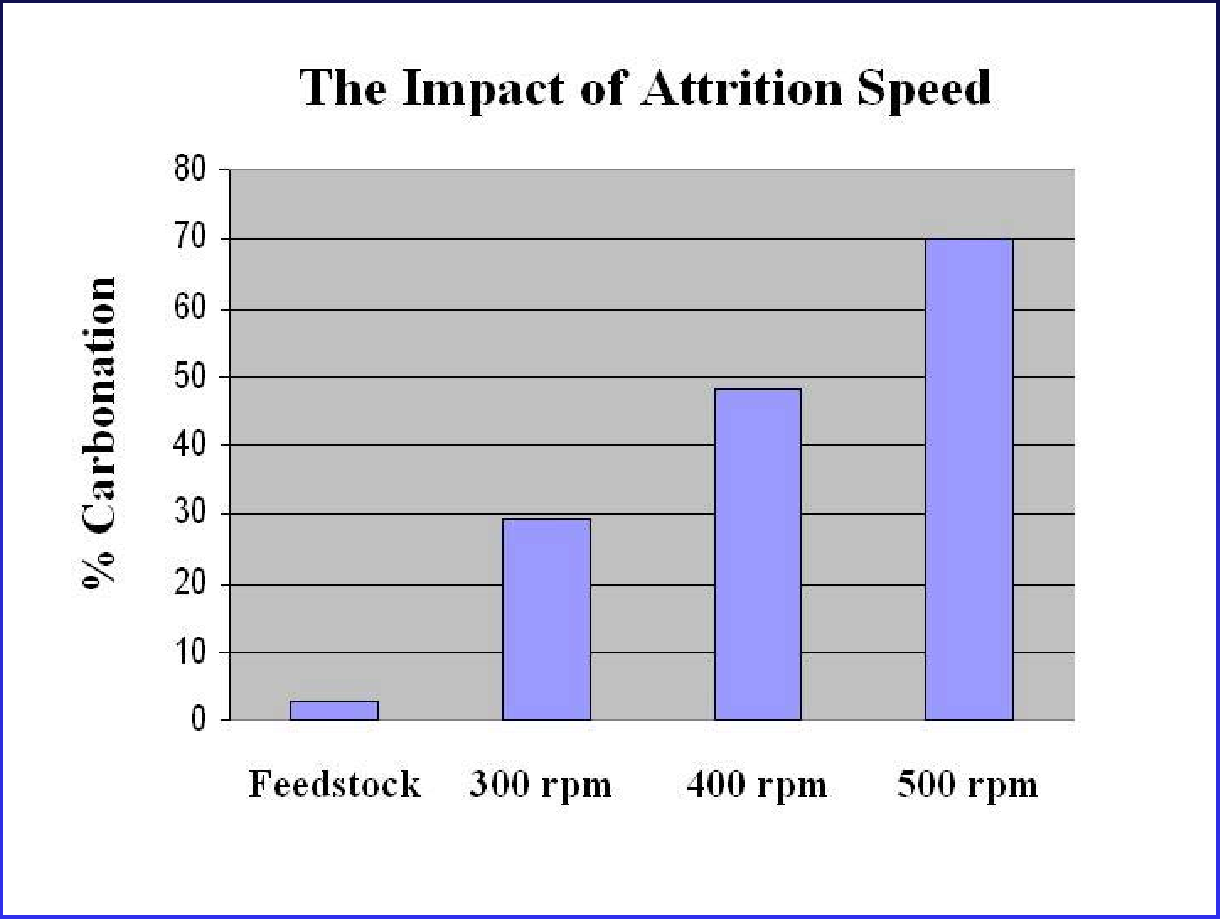
- **Reduced dehydroxylation temperature**
- **Reduced hydroxide content**
- **A new route to activated meta-serpentine formation**

THERMOMECHANICAL ACTIVATION CAPABILITY DEVELOPED AT THE ALBANY RESEARCH CENTER

Water Cooled Attritor

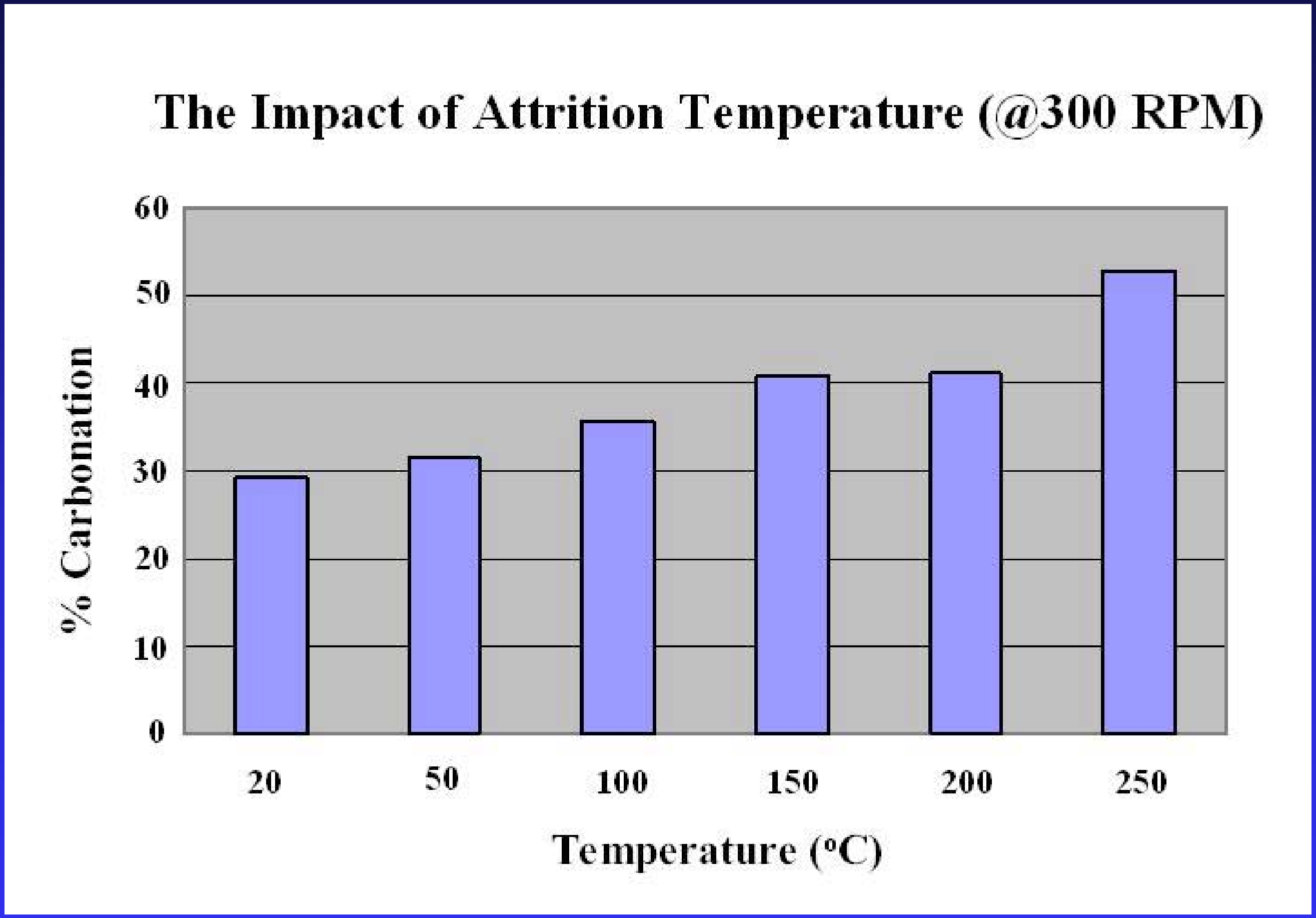
Controlled Temperature Attritor

EXTENT OF CARBONATION VS. MECHANICAL ACTIVATION AGRESSIVENESS*



* SWOL attritted for 1hr under argon, with water cooling.

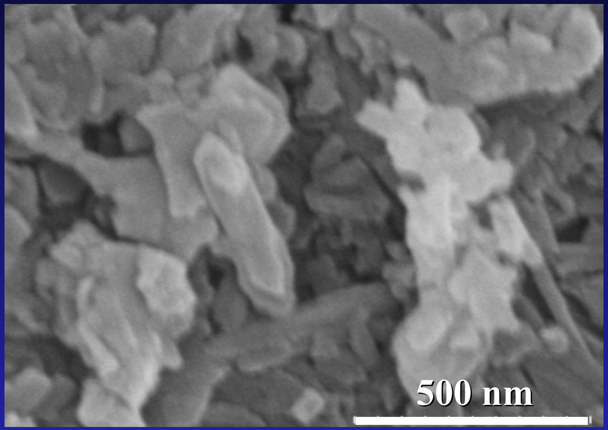
THERMOMECHANICAL ACTIVATION UNDER MODERATELY AGGRESSIVE CONDITIONS*



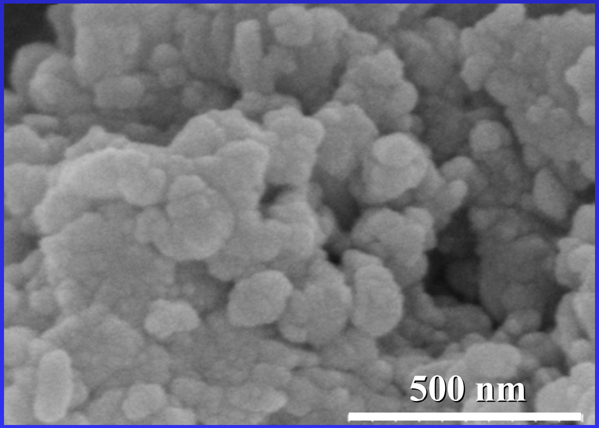
* SWOL attritted starting at the temperature shown for 1hr under argon.

WHY DOES ADDING HEAT DURING MECHANICAL ACTIVATION ENHANCE CARBONATION REACTIVITY?

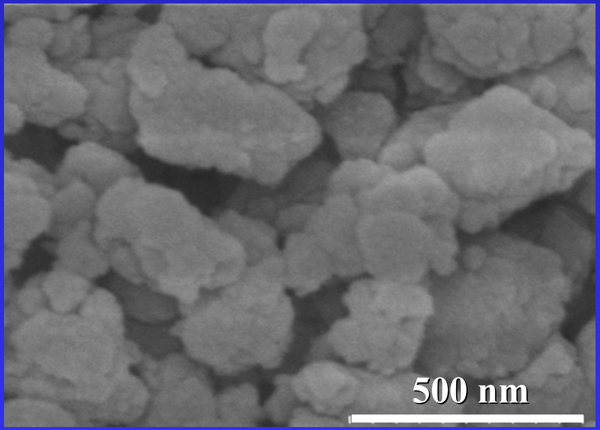
SWOL MORPHOLOGY (FESEM) AS A FUNCTION OF THERMOMECHANICAL ACTIVATION TEMPERATURE



SWOL Feedstock

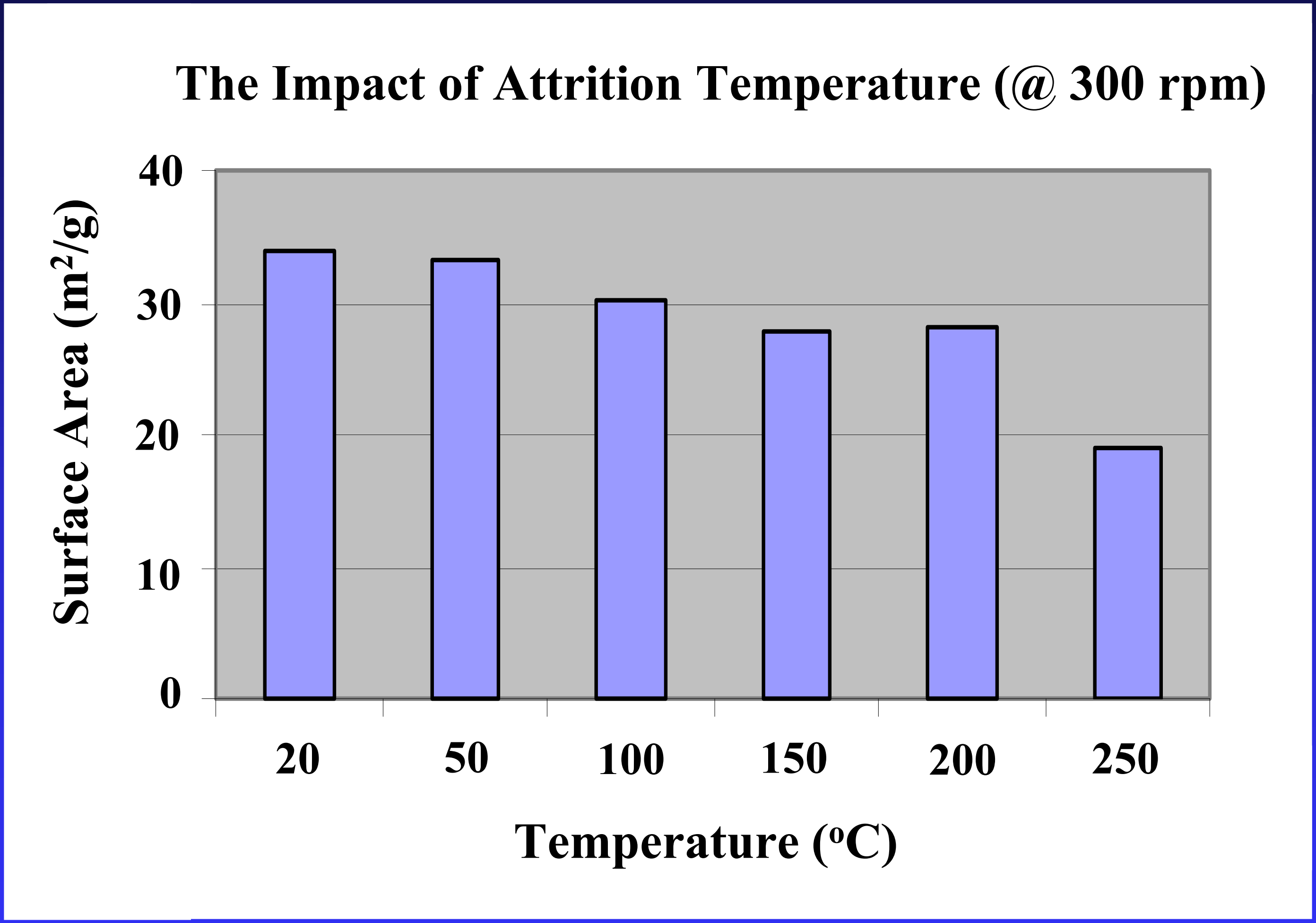


Attritted @ 20 ^{o}C and 300 rpm



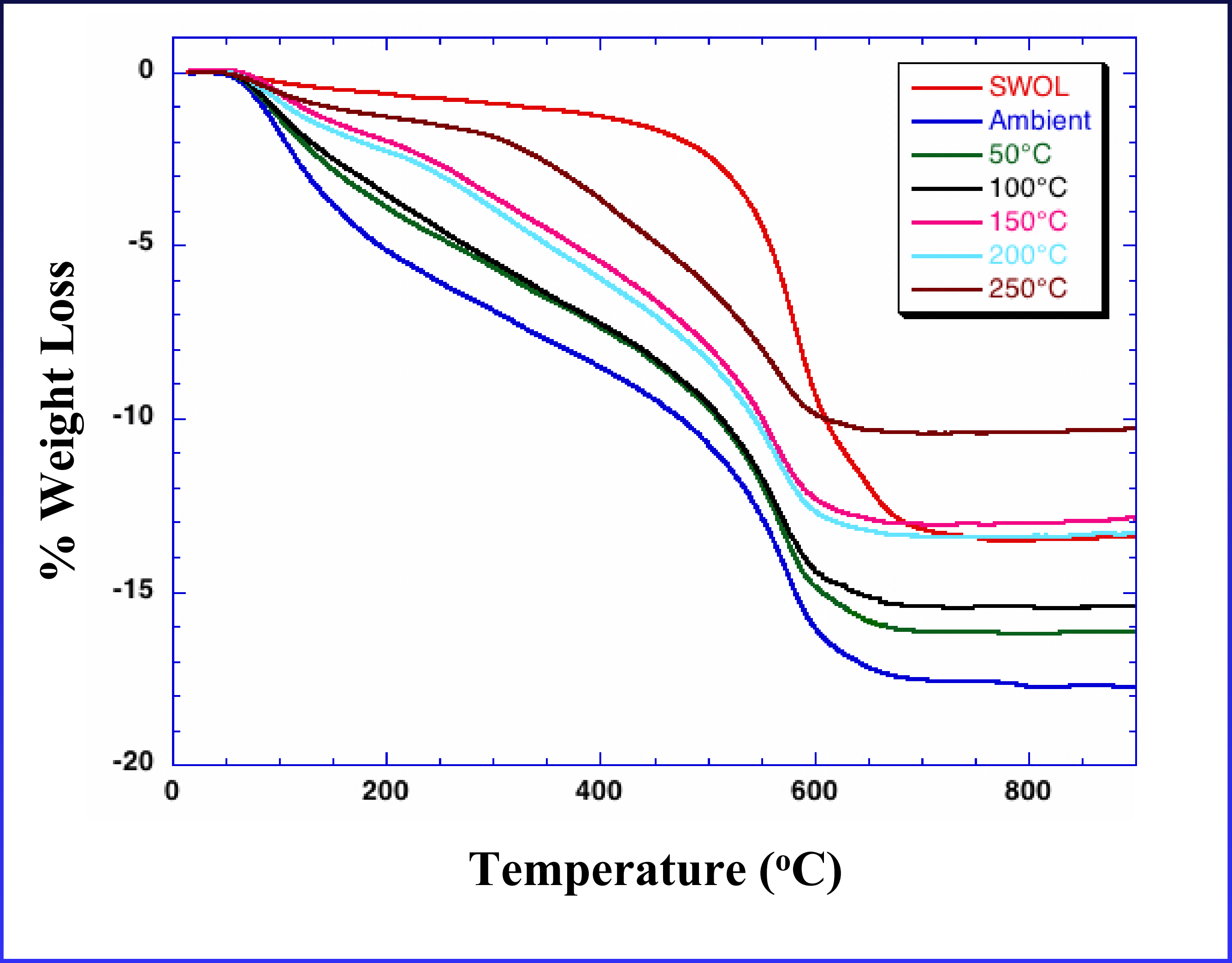
Attritted @ 250 ^{o}C and 300 rpm

SURFACE AREA AS A FUNCTION OF ACTIVATION TEMPERATURE*

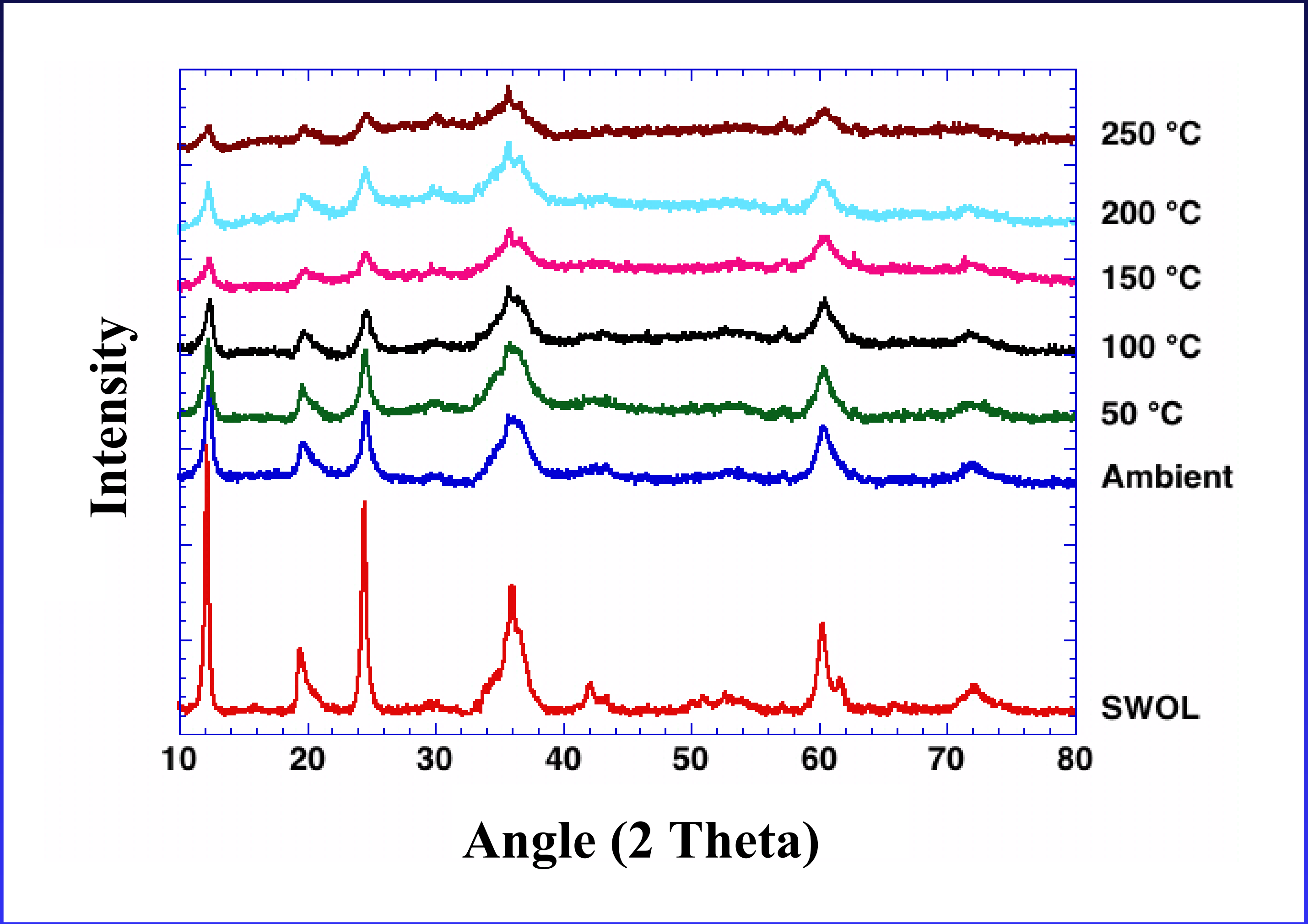


*** Based on BET measurements taken in collaboration with the Albany Research Center.**

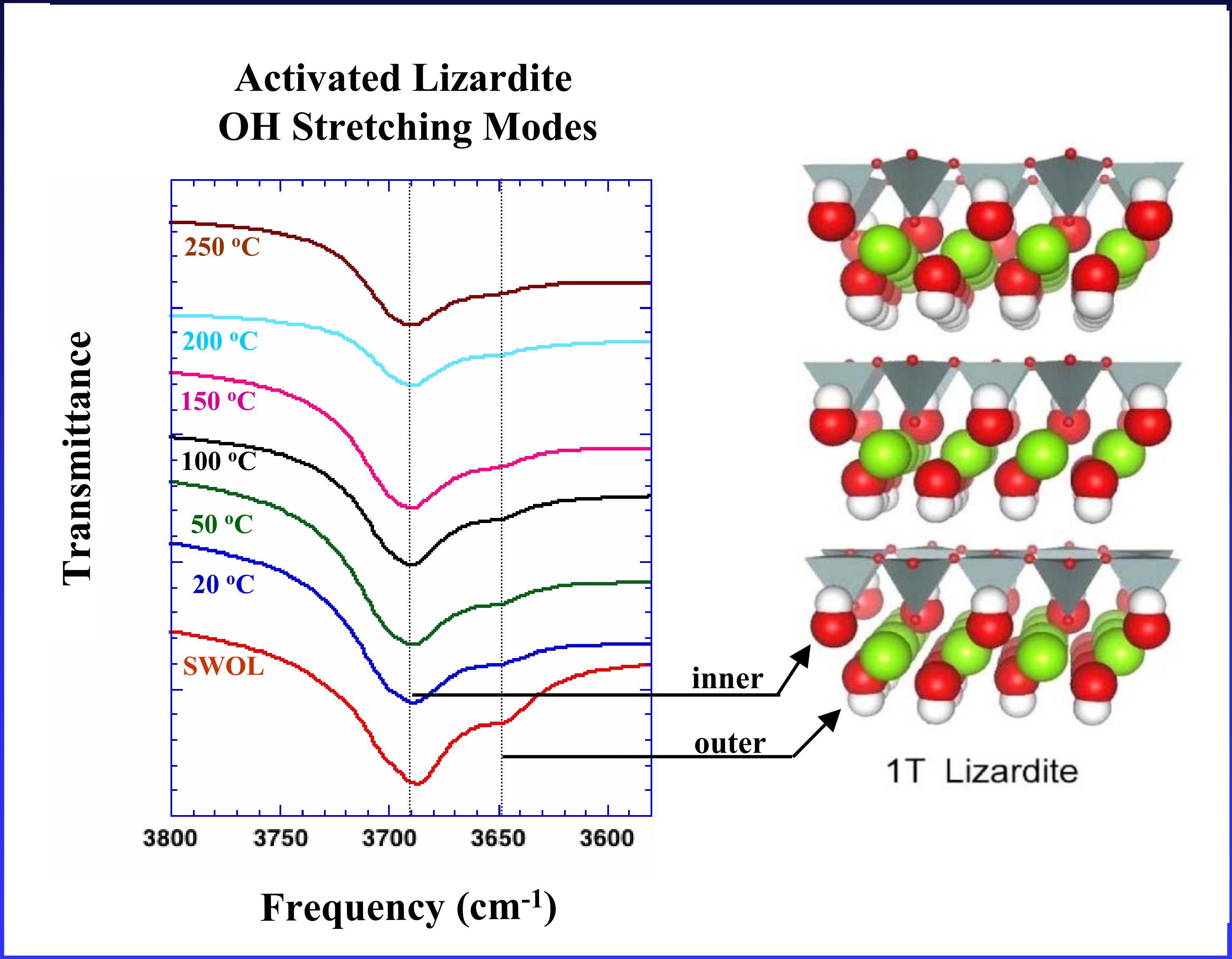
THERMOGRAVIMETRIC ANALYSIS AS A FUNCTION OF ACTIVATION TEMPERATURE



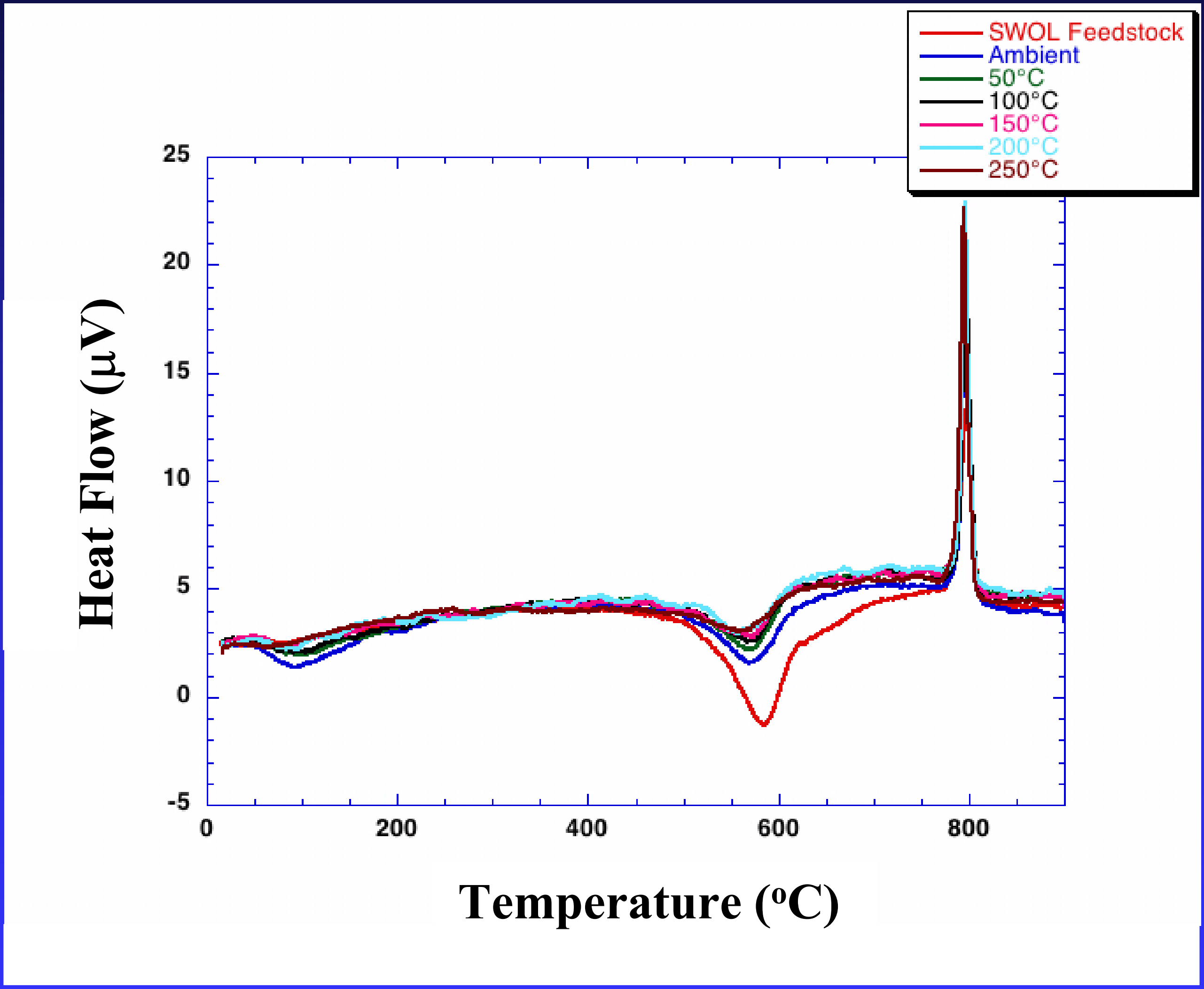
X-RAY POWDER DIFFRACTION AS A FUNCTION OF ACTIVATION TEMPERATURE*



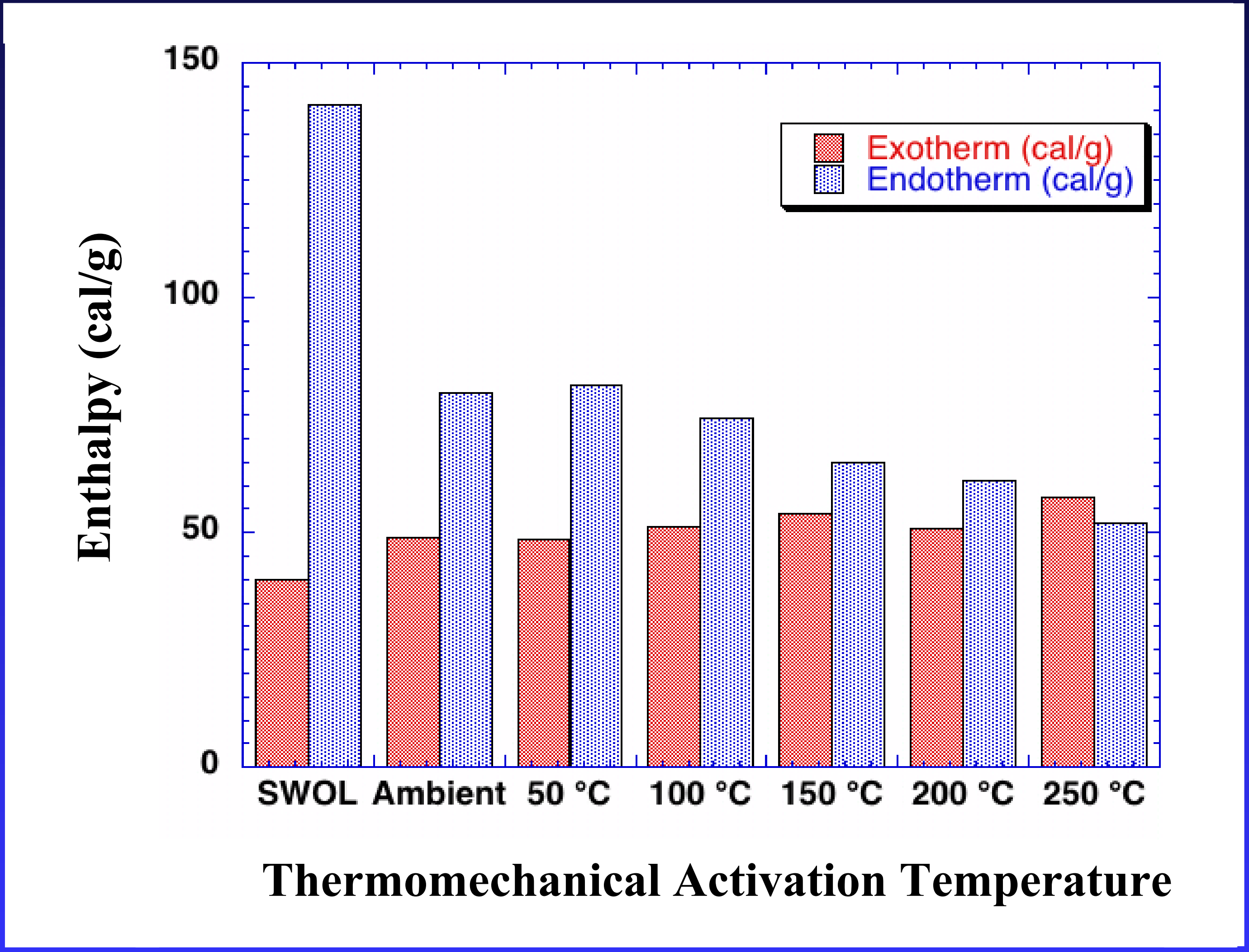
INFRARED ANALYSIS AS A FUNCTION OF ACTIVATION TEMPERATURE



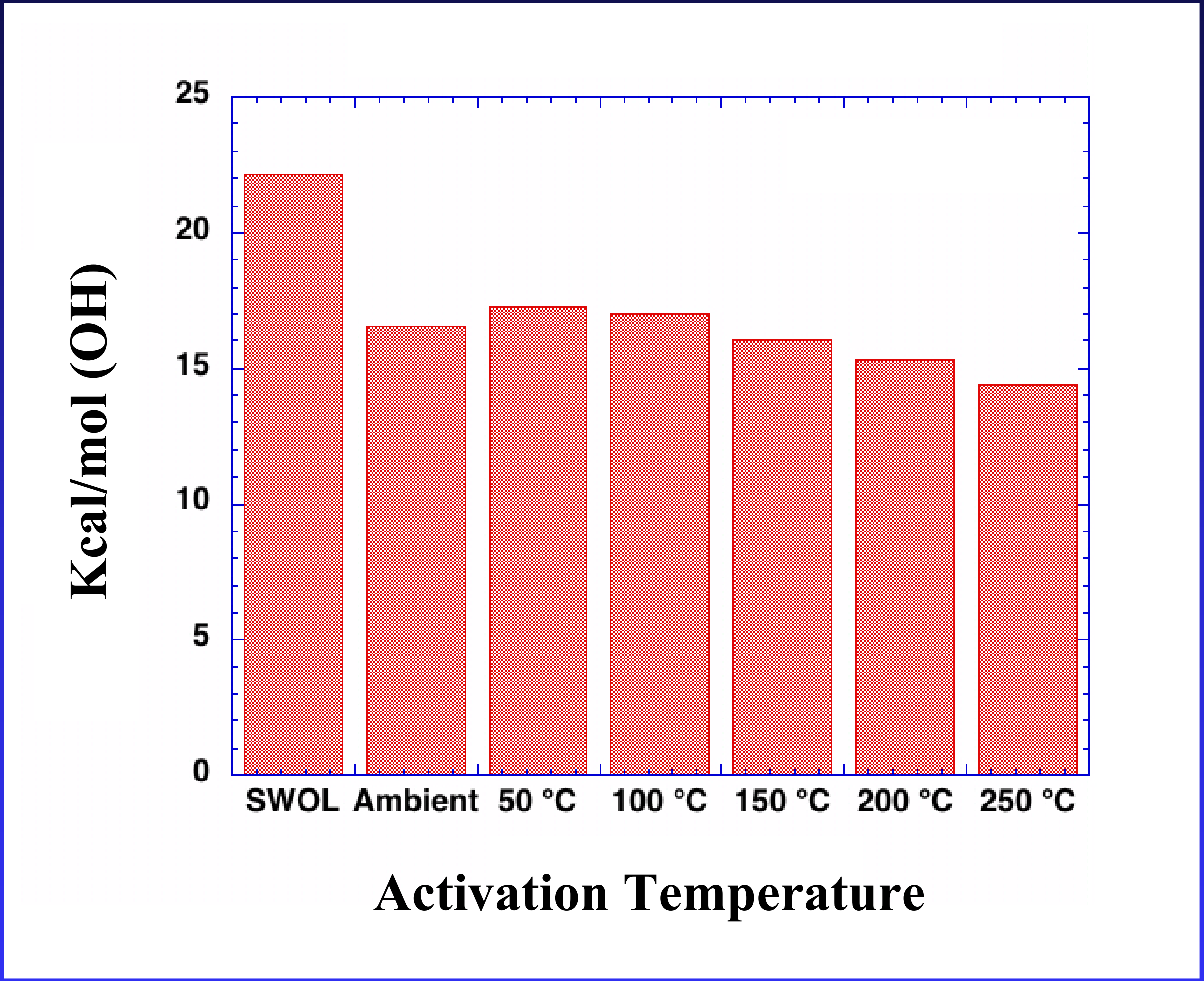
DIFFERENTIAL THERMAL ANALYSIS (DTA) AS A FUNCTION OF ACTIVATION TEMPERATURE



ENDOTHERM AND EXOTHERM ENERGIES AS A FUNCTION OF ACTIVATION TEMPERATURE



NORMALIZED DEHYDROXYLATION ENERGY AS A FUNCTION OF ACTIVATION TEMPERATURE



CONCLUSIONS

- **Initial studies have shown combining low-level "waste" heat with mechanical activation can substantially enhance lizardite carbonation reactivity.**

- **Substantial increases in the extent of carbonation have been observed in this feasibility study, indicating thermomechanical activation offers intriguing potential to lower process cost.**

- **Initial studies indicate adding low-level heat during moderately intense lizardite mechanical activation promotes its:**
  - **energy absorption during activation,**
  - **carbonation reactivity,**
  - **structural disorder, and**
  - **dehydroxylation,**

  while decreasing its:
  - **surface area, and**
  - **water absorptive capacity.**

FUTURE WORK

- Further probe the role structural disorder plays in enhancing serpentine carbonation reactivity (e.g., via detailed XPD, HRTEM, and EXAFS analysis).

- Extend these studies as a function of mechanical activation conditions. How far can we reduce process cost via thermomechanical activation?